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VI. *Observations and Experiments upon oxygenized\* and hyper-oxygenized muriatic Acid; and upon some Combinations of the muriatic Acid in its three States.* By Richard Chenevix, Esq. F. R. S. and M. R. I. A.

Read January 28, 1802.

WHEN Mr. BERTHOLLET made known the combination of what was then called oxygenated muriatic acid with potash, he gave as his opinion, that the proportion of oxygen, relatively to the quantity of acid, was greater in the salt than in uncombined oxygenized muriatic acid. This conjecture was fairly founded upon the observation, that, in his mode of preparing this salt, a large portion of common muriate was formed in the liquor, along with the hyperoxygenized muriate. The Memoir which he published in the year 1788, is the last with which I am acquainted, upon this subject. It does not contain any thing that, considering the accuracy which is now required in experiments, amounts to a demonstration of the relative proportions of oxygen, in oxygenized and hyperoxygenized muriatic acids. Unfortunately, this chemist has not pursued his researches any farther; although, from his own words, we had every reason to hope that they would have been continued.

In the *Système des Connoissances chimiques* of Mr. FOURCROY,

\* I have preferred this word to *oxygenated*, because *ate* is the appropriate termination of certain salts formed by the acids in *ic*. Some further remarks upon this subject will be made in a work now in the press, entitled *Remarks upon Chemical Nomenclature*.

we find a summary of the experiments that had preceded the impression of his work, together with the following sentence. "Tous les muriates suroxygénés sont décomposés par les acides, souvent avec une violente décrepitation, avec une dégagement de vapeur jaune verdâtre, et une odeur très-forte. Cette vapeur est de véritable acide muriatique suroxygéné. Elle est lourde, tombe en goutellettes d'un jaune vert, et forme des striés comme de l'huile, sur les corps auxquels elle adhère." This assertion carries no confirmation along with it; and does not amount so near to proof as the position of the former chemist: so that, in fact, the existence of hyperoxygenized muriatic acid, and of its combination with potash, rests, at present, upon the conjecture of Mr. BERTHOLLET; a conjecture however which, as well as his whole dissertation upon the subject, bears all the marks of genius which so strongly characterise every production of that sagacious philosopher. Some notice has been taken of other saline combinations, formed by causing a current of oxygenized muriatic acid to pass through solutions of the alkalis, or earths, or by otherwise combining them. Mess. D'OLFUS, GADOLIN, VAN-MONS, LAVOISIER, and others, have slightly mentioned some of these combinations. But, with the exception of Mr. BERTHOLLET, I know of no chemist who has approached so near to the real state of the combination of muriatic acid and oxygen with potash, as Mr. HOYLE, of Manchester. The true nature of this salt, however, is one of those things which many persons have credited without proof; and which many others have been on the eve of discovering.

I shall now proceed to lay before the Society, an account of the observations and experiments which have led me to conclude, that muriatic acid does exist in the form of oxygenized.

and hyperoxygenized muriatic acid, as announced in the title of the present communication; and that, in either state, it is capable of entering into saline combinations.

With this view, I shall describe,

1st. The means by which I think I have succeeded, in ascertaining the constituent parts, as well as the proportions, in oxygenized and hyperoxygenized muriatic acid.

2dly. I shall mention some of the combinations of the muriatic acid, in its three states.

In treating upon the first of these objects, I must in some measure anticipate the second; and must suppose some things known, which are hereafter to be described. This inconvenience is inevitable; as the natural order of things leads me to treat of the acid, before I consider the bodies into the composition of which it enters.

I exposed to the heat of a lamp, 100 grains of hyperoxygenized muriate of potash. It decrepitated gently, and in a short time melted. After remaining in fusion nearly an hour, I allowed it to cool: it crystallized as formerly, and had lost 2,5 per cent.. I increased the heat to redness, in a furnace. The salt boiled with a violent effervescence, and rapid disengagement of gaseous fluid, together with a thin white vapour, and then sunk suddenly into a white spongy mass. The loss of weight usually varied from 42 to 48 or 50 per cent.

I put 100 grains into a coated glass retort, luted to a small and perfectly dry receiver, having a tube communicating with a glass bell in the pneumatic tub. The fire had not been lighted very long, when a slight dew began to line the inside of the receiver; and, as soon as the retort was nearly red hot, a disengagement of gas, so sudden as almost to be explosive, took

place. A quantity of thin white vapour arose, which afterwards was deposited, in the form of a white sublimate, in the receiver and the tube. When the extrication of gas had ceased, the apparatus was allowed to cool. The gas, with the usual corrections of temperature and pressure, measured 112,5 cubic inches, = 38,3 grains. The 2,5 mentioned above, as the loss of this salt at a low heat, were water. 53,5 remained in the retort; and the white sublimate in the tube and receiver amounted to 5.

The products of this operation were therefore,

|                               |   |   |   |   |             |
|-------------------------------|---|---|---|---|-------------|
| Water                         | - | - | - | - | 2,5         |
| Oxygen                        | - | - | - | - | 38,3        |
| Salt in the tube and receiver |   |   |   | - | 5           |
| Salt remaining in the retort  |   |   |   | - | <u>53,5</u> |
|                               |   |   |   |   | 99,3.       |

To find the proportions of oxygen and muriatic acid, in hyperoxygenized muriatic acid, it now only remains to determine the sum of the quantities of muriatic acid, contained in the 53,5 of the retort and the 5 of the tube and receiver. The 53,5 gave, by nitrate of silver, a precipitate corresponding to 18,21; and the 5, a precipitate corresponding to 1,76; in all, 20 of muriatic acid. Therefore, 38,3 of oxygen, and 20 of muriatic acid, combine to form 58,3 of hyperoxygenized muriatic acid; or, 100 of hyperoxygenized muriatic acid contain, within a fraction,

|               |   |   |   |   |           |
|---------------|---|---|---|---|-----------|
| Oxygen        | - | - | - | - | 65        |
| Muriatic acid | - | - | - | - | <u>35</u> |
|               |   |   |   |   | 100.      |

And the elements of hyperoxygenized muriate of potash, should be thus stated:

|               |    |      |                     |   |   |            |
|---------------|----|------|---------------------|---|---|------------|
| Oxygen        | -  | 38,3 | { hyperoxygenized } | - | - | 58,3       |
| Muriatic acid | 20 |      | { muriatic acid }   |   |   |            |
| Potash        | -  | -    | -                   | - | - | 39,2       |
| Water         | -  | -    | -                   | - | - | <u>2,5</u> |
|               |    |      |                     |   |   | 100,0.     |

It may be observed, that the 53.5 of the retort did not yield the same proportion of acid as the 5 of the tube and receiver. The fact is, that all muriates lose a little of their acid at a red heat, as I shall presently mention more particularly; and the small loss was, in all probability, owing to a portion of acid disengaged by the heat to which the salt was necessarily exposed during the operation.

Having thus ascertained the proportion of oxygen in hyperoxygenized muriatic acid, by means of its combination with potash, a ready method occurred to arrive at the knowledge of that contained in oxygenized muriatic acid. For this purpose, I disposed in the following manner, a Woulfe's apparatus, consisting of three bottles, and connected with the pneumatic tub. In the first bottle, I put a solution of potash,\* in about six parts of water. In the second, a solution of the same; but so dilute, as that no part of the salt, which might be formed, should crystallize during the operation. About twenty parts of water was the proportion there employed. In the third bottle, I put common carbonate of potash. Through this apparatus, I sent a current of oxygenized muriatic acid, disengaged by sulphuric acid, from a mixture of muriate of soda and black oxide of manganese, in the well known manner. Crystals of hyperoxygenized muriate of potash were formed in the liquor of the first bottle; and, as long as they remained, I was certain, from previous experiment, that no sulphuric or muriatic acid could pass into the second bottle. The current was continued, till the liquor of that bottle contained an excess of acid. The carbonate of potash, in the third bottle, absorbed the superabundant vapours; and the

\* Whenever potash, soda, barytes, an acid, an alkali, water, or the names of other substances are used without an epithet, they are meant to denote them in that state which is commonly called *pure*.

pneumatic apparatus was ready to collect any gases that might be evolved. By these means, I obtained, in the second bottle, a solution of whatever substance might result from the action of potash upon hyperoxygenized muriatic acid.

I took a portion of this liquor, which I shall call *entire liquor*,\* and distilled it to dryness in a glass retort, taking care to screen it from light. A tube from the receiver communicated with the pneumatic tub. My object was to ascertain, whether the change observed by Mr. BERTHOLLET, in the distribution of the elements of oxygenized muriatic acid, to form, with potash, a simple and a hyperoxygenized muriate, really took place among those elements themselves, independently of any absorption of oxygen from the atmosphere, or extrication of it from the salt. Nothing but some water, and a few inches of the dilated air of the vessels, passed into the receiver and the pneumatic apparatus; and I found, in the retort, a saline mass,† perfectly dry and crystallized. Hence it is evident, that the same quantity of oxygen as that formerly contained in the oxygenized muriatic acid, which had been united to the alkali, to form the total mass of salt, was now condensed, in that part which had become hyperoxygenized muriate.

To ascertain this quantity, I dissolved 100 grains of the entire salt in water, and precipitated by nitrate of silver. I thus obtained a quantity of muriate of silver, which, by proportions previously determined, I knew to correspond to 84 of muriate

\* I am well aware that, upon philosophical principles, this appellation is objectionable; but, for the sake of brevity, I have used it as a temporary name, for a substance which has only a relative existence among chemical bodies.

† This salt, I shall call *entire salt*.

of potash: therefore, 16 were hyperoxygenized muriate of potash.\* But, according to the proportions established above in hyperoxygenized muriate of potash, 16 of this salt contain 6 of oxygen, with 3,20 of acid, the remainder being alkali and water; and, by preliminary experiments, I found that 84 of muriate of potash contained 27,88 of muriatic acid. Therefore,  $27,88 + 3,20 = 31,08$  of muriatic acid, with 6 of oxygen, or, to reduce it to the quintal,

|               |   |   |   |       |
|---------------|---|---|---|-------|
| Muriatic acid | - | - | - | 84    |
| Oxygen        | - | - | - | 16    |
|               |   |   |   | <hr/> |

100, are the proportions

which combine to form oxygenized muriatic acid.

To corroborate this evidence, I distilled 100 grains of the entire salt mentioned above; and obtained nearly 16,5 cubic inches of oxygen gas; which as accurately corresponds with the trial by nitrate of silver, as can be expected in experiments of this nature.

Mr. BERTHOLLET, in his Memoir upon oxygenized muriatic acid, gives, if I understand him rightly, the following statement of the proportions, and of the means by which he obtained his results. He exposed to the light of the sun, 50 cubic inches of water, saturated with oxygenized muriatic acid; and collected in the pneumatic tub, 15 cubic inches of oxygen gas. I here neglect fractions; because our results appear, at first sight, to differ so widely as not to require great accuracy in giving their comparative statement. He then preci-

\* I must observe here, that hyperoxygenised muriate of potash does not, like simple muriate, decompose the salts of silver. This shall be further animadverted upon, and proved, in its proper place.



pitated, by nitrate of silver, the 50 cubic inches of liquor, which had become simple muriatic acid, and obtained 38,3 grains of muriate of silver. But, by experiments, I found that 38,3 of muriate of silver contain 65 of muriatic acid. Therefore, 65 of muriatic acid combine with 15 cubic inches\* (= 8 grains) of oxygen, to form 73 of oxygenized muriatic acid. But  $73 : 8 :: 100 : 11$ , or nearly. For this difference, however, it may be easy to account. Perhaps Mr. BERTHOLLET's 50 cubic inches of oxygenized muriatic acid, contained originally a little simple muriatic acid; and he says besides, that he suspects all the oxygen was not disengaged. This indeed is most probable; and I am happy that I can reconcile the proportions which I have found, to the opinion of so skilful a chemist.

Mr. CRUIKSHANK likewise, in his additional Observations upon Hydrocarbonates, has stated that 2,3 parts of oxygenized muriatic acid contain 1 of oxygen, or about 43,5 per cent. But this able chemist, to whom we are indebted for the discovery of the gaseous oxide of carbone, procured his oxygenized muriatic acid by a peculiar method, which I shall notice, in speaking of the action of acids upon hyperoxygenized muriate of potash. The substance he obtained was, in fact, not oxygenized muriatic acid gas, but a mixture of that gas with hyperoxygenized muriatic acid. I have not the smallest doubt of the accuracy of his statement; but, being the proportion of a mixture, it in no way contradicts either of those I have determined in this Paper.

Before I dismiss this part of the subject, I wish to anticipate an objection, founded upon an observation of Mr. BERTHOLLET, which may be made to the above experiments. He says, that when the alkaline solution is very concentrate, an effervescence

\* Mr. BERTHOLLET's proportions are in the old French weights and measures.

takes place during the whole of the saturation, and for some days after; and this effervescence, he attributes to the escape of oxygen. But I have already said, that no oxygen gas was disengaged in any part of my process; and no effervescence took place in any of the bottles, except the third; so that, no superabundance of oxygen could have passed from one into the other, nor could any diminution of the total quantity have been produced. By repeating the experiments, sometimes with a solution of alkali, and sometimes with water alone, in the first bottle, I obtained the liquor in the second bottle uniform in all cases. Indeed, as potash prepared in Mr. BERTHOLLET's manner, was not in such general use at the time he performed his experiments as at present, I suspect that a great part of this effervescence was owing to a disengagement of carbonic acid from the alkali.

Having thus proved the difference between the states of these two acids, I shall now proceed to the combination of each with salifiable bases.

#### OXYGENIZED MURIATES.

As many properties of the entire liquor, before it had been evaporated to dryness, had led me to imagine that the acid was united with the alkali, and remained in combination with it, in the state of oxygenized muriatic acid, till the moment of crystallization, I think it necessary to state at length the appearances which induced me to draw that conclusion, and the experiments which afterwards convinced me that it was erroneous.

A few drops of sulphuric acid, poured into some of the entire liquor, caused an effervescence, and a smell of hyperoxygenized muriatic acid.

Very strong acetic acid produced the same effect.

By other experiments, I had ascertained that acetic acid could not decompose any part of the entire salt; and hence I concluded, that in the entire liquor, before evaporation, some of the salt remained in the state of oxygenized muriate, the acid of which was expelled by the sulphuric or acetic acid; and, that it was not till the moment of crystallization, that the elements of the salt underwent a total resolution into muriate, and hyperoxygenized muriate, of potash. However, a small quantity of any of the very soluble neutral salts, such as nitrate or muriate of ammonia, or even a little alcohol, produced the same effects; and I was then convinced, that the effervescence was owing to some uncombined oxygenized muriatic acid gas, remaining in the liquor; and which was disengaged, in proportion as the water was taken from it, by the superior affinity of the salt, or the alcohol, I had used.

By some previous experiments, I had ascertained, as I have just mentioned, that acetic or acetous acids do not decompose hyperoxygenized muriate of potash. I sent a current of oxygenized muriatic acid through a solution of acetite of potash; and, upon evaporation, I found that the acetous acid had been disengaged, and that muriate, with hyperoxygenized muriate, of potash had been formed. But, from some trials, which I shall presently relate, I was induced to believe, that oxygenized muriatic acid attracts the salifiable bases with a much weaker affinity than acetous acid. It is well known that the contact of oxygenized muriatic acid with an alkali, is sufficient to produce a combination of that acid with the alkali; and, from the last-mentioned experiments it appears, that it is not absolutely necessary that

the alkali should be in a free state. If it be combined with an acid weaker than hyperoxygenized muriatic acid, the original acid will be expelled; and muriate and hyperoxygenized muriate will be formed, as if the alkali had been free.

As a further proof, that the change in the distribution of oxygenized muriate of potash takes place at the moment of contact of the acid and the alkali, and consequently long before the crystallization, I mention the following experiments.

I precipitated, by nitrate of silver, 400 grains of the entire liquor, previously to its being evaporated; and obtained 71 grains of muriate of silver.

I evaporated to dryness, 400 grains of the same liquor, redissolved the residuum, and, by dropping in nitrate of silver, obtained 70 grains of muriate. The difference of one grain, in these experiments, does not amount to 0,2 of a grain of muriate of silver; and ought not to be regarded.

From these experiments, it is past all doubt, that the original entire liquor did not contain oxygenized muriate of potash. For, if such a combination had existed in it, I should have obtained a smaller portion of muriate of silver in the first than in the second case, on account of the total separation into muriate and hyperoxygenized muriate having not yet taken place.

We are not however to conclude, from these experiments, that there are no such things as oxygenized muriates. Although they cannot be exhibited in a palpable state, it is easy to demonstrate that they do really exist. I shall prove, in the proper place, that hyperoxygenized muriate of ammonia is not an incompatible combination; and must, for the present, assume the datum, in order that I may demonstrate the necessary

existence of oxygenized muriates. Therefore: If muriatic acid, or if hyperoxygenized muriatic acid, be brought in contact with ammonia, the result will be muriate, or hyperoxygenized muriate, of ammonia. But, if the acid, disengaged by sulphuric acid, from a mixture of black oxide of manganese and muriate of soda, be sent through ammonia, both are decomposed. Hence it is evident, that the acid combines with the alkalis, in the state of oxygenized muriatic acid; and that the separation into muriate and hyperoxygenized muriate, is produced by a subsequent action, among the elements of oxygenized muriate of potash.

Upon the whole, it appears to me fair to conclude,

1st. That the salts of this genus do really exist, previous to the formation of hyperoxygenized muriate of potash.

2d. That the affinity exercised by hyperoxygenized muriatic acid for ammonia, and (by very strong analogy) for the other bases, is much greater than that of oxygenized muriatic acid. For, hyperoxygenized muriatic acid, as shall presently be shewn, having a much more powerful action upon all combustible bodies, whether simple or compound, than oxygenized muriatic acid, it would be natural to suppose that the former acid would act more powerfully upon the inflammable element of ammonia. But oxygenized muriatic acid combines with the hydrogen of that alkali; which, however, is not decomposed by hyperoxygenized muriatic acid; yet the affinity of hyperoxygenized muriatic acid for ammonia, is the only cause that determines the union of the acid and the alkali, without decomposition. But these affinities shall be more fully treated of, in speaking of hyperoxygenized muriate of ammonia.

## ALKALINE AND EARTHY HYPEROXYGENIZED MURIATES.

*Generic Characters.*

Hyperoxygenized muriates are formed by passing a current of oxygenized muriatic acid through the basis, dissolved or suspended in water, as in the formation of the last mentioned genus. Their first formation is owing to the separation of the elements of an oxygenized muriate, into hyperoxygenized muriate and simple muriate; from which latter, they may be separated by crystallization, or by another process, which I shall mention, in treating of the earthy hyperoxygenized muriates. By simple trituration, they scintillate, with noise. They are decomposed by a low red heat; and give out a considerable quantity of oxygen, as they become simple muriates. They cannot be brought down, by any means that I have tried, to that diminished state of oxygenizement, which would constitute oxygenized muriates. They inflame all combustible bodies with violence, as is well known. They are soluble in water; many of them, in alcohol; and some are deliquescent. The acid is expelled, with particular phenomena, by sulphuric, nitric, and muriatic acids, without heat; and, a little below a boiling heat, by phosphoric, oxalic, tartareous, citric, and arsenic acids: but they are not acted upon by benzoic, acetic, acetous, boracic, prussic, or carbonic acids. Those vegetable acids which are powerful enough to decompose them, give out, towards the end, a gas of a peculiar nature, which has not so much smell as oxygenized muriatic acid gas, but which affects the eyes in an extraordinary manner, and promotes an uncommon and rather painful secretion of tears. I have not yet examined this gas, as there was invariably an inflammation of the mixture, with explosion and rupture of the

vessels, almost as soon as it began to be evolved. When pure, the hyperoxygenized muriates do not precipitate any of the metallic salts, although I believe they decompose some. The order in which the bases seem to be attracted by the acid, is, potash, soda, barytes, strontia, lime, ammonia, magnesia, alumina, silica. The other earths I have not tried, and but few of the metallic oxides.

*1st Species. Hyperoxygenized Muriate of Potash.*

This salt is the best known of all the saline combinations of this acid. It has been erroneously considered as simply oxygenized, for its acid is really hyperoxygenized. It is soluble in about sixteen parts of cold water, but in much less of warm; and is easily separated, by crystallization, from muriate of potash. Alcohol can dissolve a small portion of it. It seems capable of existing in more states than one; for, in passing a current of oxygenized muriatic acid, very slowly, and in the dark, through a solution of potash, till saturated, I have obtained flexible and shining needle-like crystals. This leads me to suspect, either a hyperoxygenized muriate of potash with excess of acid, or that acid with a superaddition of oxygen. It would be superfluous to enter into a minute description of a substance so well known as hyperoxygenized muriate of potash; but, it being the substance whence I have chiefly attempted to disengage the acid, I shall enter into a particular detail of the action of the more powerful acids upon this salt.

If concentrate sulphuric acid be poured upon hyperoxygenized muriate of potash, a violent decrepitation, sometimes but rarely accompanied by a flash, takes place. A thick heavy vapour, of a greenish yellow colour, which rises with difficulty to the top of the vessel, if it be deep, is disengaged. The smell is not altogether

unlike nitrous gas ; but is peculiarly fetid, and may be compared to that which is emitted by brick-kilns, mixed with that of nitrous gas. It differs much from oxygenized muriatic acid gas ; the latter being pungent and penetrating, the other heavy and oppressive ; and it does not produce, at least in so great a degree, the catarrhal symptoms caused by the other. At the bottom of this vapour is a bright orange-coloured liquor, which has the same smell as the vapour. This is the acid contained in the salt ; and I have proved it to be hyperoxygenized muriatic acid. But, although the salt from which the acid is disengaged be pure, the acid itself is never so ; because the very act of disengaging it effects its decomposition, and some of it is converted into oxygenized muriatic acid. The colour of litmus paper, on this account, is generally destroyed by the liquor. I say on this account, because I have some reason to believe, from having observed this not to be uniformly the case, that hyperoxygenized muriatic acid reddens the vegetable blues. However, it must be considered, that the sulphuric acid used to disengage the hyperoxygenized muriatic acid is still present ; and we can draw no certain conclusion, until we have obtained this acid free from all other substances. If to this mixture of hyperoxygenized muriate of potash and sulphuric acid, heat be applied, an exceedingly violent explosion, with a white and vivid flash, takes place, before the liquor has attained the temperature of 125 of FAHRENHEIT. In order to obtain this acid, I attempted to distil 500 grains, in a glass retort, in a water bath, with every precaution against such accidents as I could not but in some measure expect ; when, almost as soon as I had kindled the fire, I saw, in the bottom of the retort, an extremely white, vivid, and rapid flash, which was immediately followed by a loud report. The retort was reduced almost to



powder; so that scarcely any fragments of it could be found in the laboratory. The windows, and several glass vessels, were broken. I happened to be holding the neck of the retort, at the moment of the explosion, yet received no injury, except a slight contusion in the hand. But Dr. VANDIER, a French gentleman of considerable chemical and medical talents, to whom I am indebted for much able assistance in my laboratory, was wounded in several places; particularly, the tunica conjunctiva of the eye was so lacerated, that a piece of it hung down, and, by getting under the inferior eyelid, caused the most painful irritation, and endangered his sight. One of the frontal arteries also was divided. I relate these circumstances thus fully, as the most effectual means of putting upon their guard, those who would repeat the experiment. If the sulphuric acid be dilute, heat may be applied with more safety; and the phenomena are different. The hyperoxygenized muriatic acid is disengaged from the basis; but, as the heat requisite to distil the acid is more than sufficient to decompose it, oxygenized muriatic acid comes over with it; and oxygen gas is collected in the pneumatic tub. If the distillation be continued, the same danger arises as in the former case, because the sulphuric acid becomes concentrated; and it would seem, that its action upon the salt is slight and partial at a low temperature, but violent and instantaneous when heated and concentrate. I could not, therefore hope, by these means, to obtain the acid disengaged and pure.

If the manner of bringing the sulphuric acid and the salt into contact be reversed, and the salt be dropped into the acid, the yellow vapours and the orange-coloured liquor are produced, but generally without decrepitation. If they be allowed to remain some days in contact, the vapours continue, and oxygen gas is constantly disengaged, even in the common light of the

day, and at the temperature of the atmosphere. By cooling the first receiver with ice, I thought that I had once obtained this acid crystallized in the form of four-sided pyramids, of an orange colour. But, though I really believe this to have been the case, I do not positively affirm it.

Nitric acid produces nearly the same phenomena; but the smell and other properties are rather less distinct and marked, than with sulphuric acid.

Muriatic acid decomposes this salt, and unites to its basis; but neither the yellow vapours, nor the orange-coloured liquor, are produced. The circumstances which attend the contact of the acid and the salt, are as follows. If no more muriatic acid be present than is merely necessary to decompose the salt, I do not doubt that hyperoxygenized muriatic acid will be driven off, as little decomposed as with the other acids, supposing the action to be instantaneous; but, during the contact of these two bodies, the acid expelled must meet muriatic acid not yet combined, and, uniting with it, always forms a portion of oxygenized muriatic acid. The quantity of the last acid must vary, according to the quantity of muriatic acid employed, and not combined with the alkali. It was by this method that Mr. CRUICKSHANK obtained the muriatic acid gas, which he stated to contain 43,5 per cent. of oxygen.

Phosphoric and arsenic acids do not act upon this salt, till heated with it; and then much oxygen gas is evolved. These, therefore, afford no better method of disengaging hyperoxygenized muriatic acid without decomposition.

Oxalic, tartareous, and citric acids, act as I before mentioned; and the hyperoxygenized muriatic acid holds its place, in the order of affinities for potash, immediately before the benzoic.

I shall not stop to detail a number of amusing phenomena that may be produced, by projecting into the stronger acids, mixtures of combustible bodies, whether metallic or not, and hyperoxygenized muriate of potash. The cause of them is well understood, and the theory points them out: they are, therefore, no longer objects of philosophical admiration. But I must mention one experiment, which, had it succeeded, I should have thought important. I projected various mixtures of very minutely pulverised diamond and this salt, into the different acids; but found the diamond undiminished, by every attempt to combine it with oxygen in the humid way.\*

Another, but imponderable, part of this salt, as indeed of all hyperoxygenized muriates, seems to be an extraordinary quantity of caloric. For, during their formation, scarcely any heat is disengaged, as by other acids; and, very little heat applied to the salts, gives the gaseous form to their oxygen.

An opinion has prevailed among some ingenious chemists, that, from a mixture of this salt with sulphuric acid, nitrous gas is disengaged, and sulphate of lime formed in the retort. But this is a mistake, arising, on the one hand, from the smell and vapour of the hyperoxygenized muriatic acid, and, on the other, from sulphate of lead, which the common sulphuric acid of this

\* I must confess, that the vivid flashes of light, emitted from the mixture of this salt and combustible bodies thrown into an acid, appear to me, in some measure, to prove the modification proposed by LEONHARDI, RICHTER, GREN, &c. to that part of the LAVOISIERIAN theory which regards the emission of light during combustion. Another testimony in favour of their modification, may be drawn from the vegetable kingdom. All plants growing in places deprived of light, are merely mucilaginous. But the mucilage of these plants burns without the emission of light. Light, therefore, appears not to be disengaged from oxygen; else, why not by this mucilage, as well as by other combustible bodies?

country frequently contains in solution, and which is precipitated from it by water. Before we assert a fact, we should be well assured of the pureness of our chemical agents. This supposed conversion of muriatic or hyperoxygenized muriatic acid into nitrous gas, will not pass for a decomposition, or a transmutation, of that refractory radical; and the idea of the change of potash into lime, is as erroneous as some other late assertions respecting the decomposition of the alkalis.

The proportions of this salt are, as I before stated,

|                               |   |   |              |
|-------------------------------|---|---|--------------|
| Hyperoxygenized muriatic acid | - | - | 58,3         |
| Potash                        | - | - | 39,2         |
| Water                         | - | - | 2,5          |
|                               |   |   | <hr/> 100,0. |

*2d Species. Hyperoxygenized Muriate of Soda.*

This salt is prepared in the same manner, and with the same phenomena, as the former. It is extremely difficult to obtain it pure, as it has nearly the same degree of solubility in water as muriate of soda. It is soluble in three parts of cold, and less of warm water; and is slightly deliquescent. It is soluble in alcohol; but this property alone is not sufficient to enable us to obtain it free from the muriate of soda, formed along with it in the entire liquor; as the latter salt, contrary to the assertions of all authors, is soluble in alcohol, and seems to be much more so, when accompanied by the hyperoxygenized muriate. It was by taking a large quantity of the entire salt, formed by sending a current of oxygenized muriatic acid gas through a solution of carbonate of soda, and repeatedly crystallizing in alcohol, that, with great difficulty, I obtained a little pure hyperoxygenized muriate of soda. It crystallizes in cubes, or in rhomboids little

different from cubes. It produces a sensation of cold in the mouth; and its taste is easily distinguished from muriate of soda. It is decomposed by heat, by combustible bodies, and by acids, in the same manner as the former species; and the acid holds its place for soda, as for potash, immediately before the benzoic. The basis is separated by potash only. This salt is composed of,

|                               |   |   |   |              |
|-------------------------------|---|---|---|--------------|
| Hyperoxygenized muriatic acid | - | - | - | 66,2         |
| Soda                          | - | - | - | 29,6         |
| Water                         | - | - | - | 4,2          |
|                               |   |   |   | <hr/> 100,0. |

*3d Species. Hyperoxygenized Muriate of Barytes.*

The earthy bases seem to follow, in the order of affinities for this acid, at a great distance from the alkalis. They are all superseded by the two just mentioned; and it is much more difficult to accomplish their union with the acid, than is the case with potash or soda. The most advantageous method is, to pour warm water upon a large quantity of this earth, procured by Mr. VAUQUELIN's method; and to cause a current of oxygenized muriatic acid to pass through the liquor, kept warm; so that the barytes already dissolved being saturated, a fresh portion of it may be taken up by the water, and presented in a state of great division to the acid. This salt is soluble in about four parts of cold, and less of warm water. It crystallizes like the muriate of this earth; and resembles it so much in solubility, that I could not separate them effectually by crystallization repeated several times. At first, indeed, I despaired of ever obtaining any of the earthy hyperoxygenized muriates in a state sufficiently pure for analysis. If we consider them as a genus distinct from the alkaline hyperoxygenized muriates,

a leading character may be, their great resemblance to their respective species of earthy muriates. I thought, however, that I might, if not by direct, at least by double affinity, decompose the one without the other; and phosphate of silver occurred to me as the most likely agent. If phosphate of silver be boiled with muriate of lime, of barytes, &c. a double decomposition ensues; and muriate of silver, together with phosphate of the earth, both insoluble, are precipitated. To increase the action, the phosphate of silver may be dissolved in a weak acid, such as the acetous; and, though the earthy phosphate be at first retained in solution, it will be separated by expelling the acid. The only condition absolutely necessary is, that the silver employed be free from copper. For, in preparing phosphate of silver by phosphate of soda, and by nitrate of silver thus impure, copper would be thrown down by the phosphoric acid; and the phosphate of copper would be afterwards decomposed by muriate of lime. Muriate of copper would therefore remain with the earthy hyperoxygenized muriates; or, what is still worse, a part of the muriatic acid being easily expelled from oxide of copper, the hyperoxygenized muriatic acid would be driven off from its basis, by the more powerful agency of the former. This salt has all the properties enumerated as belonging to the genus of hyperoxygenized muriates; and, with heat, the acid is expelled by all acids above the benzoic. I had hoped that, without distillation, I could procure the acid from the salt by means of sulphuric acid, which would have left an insoluble salt with barytes; but hyperoxygenized muriatic acid is so easily decomposed by light, that I have not yet obtained it, to my satisfaction, disengaged and pure. A fact well worthy of attention is, that the stronger acids disengage this acid with a flash of light,

more frequently from the earthy than from the alkaline hyperoxygenized muriates; a phenomenon which, I suppose, depends upon the relative proportionate affinities, and consequently the greater rapidity of the disengagement. But, where all is hypothesis, it is useless to draw any inference from a single fact.

The proportions of this salt are,

|                               |   |   |        |
|-------------------------------|---|---|--------|
| Hyperoxygenized muriatic acid | - | - | 47     |
| Barytes                       | - | - | 42,2   |
| Water                         | - | - | 10,8   |
|                               |   |   | <hr/>  |
|                               |   |   | 100,0. |

*4th Species. Hyperoxygenized Muriate of Strontia.*

The foregoing observations apply to the formation of this salt, to the mode of obtaining it pure by phosphate of silver, to its conduct with the acids, to the rank of its acid in the order of affinities, and to its other properties. It is deliquescent; and more soluble in alcohol than muriate of strontia. It melts in the mouth immediately, and produces cold. Its crystals assume the shape of needles.

It is composed of,

|                               |   |   |       |
|-------------------------------|---|---|-------|
| Hyperoxygenized muriatic acid | - | - | 46    |
| Strontia                      | - | - | 26    |
| Water                         | - | - | 28    |
|                               |   |   | <hr/> |
|                               |   |   | 100.  |

*5th Species. Hyperoxygenized Muriate of Lime.*

This salt is obtained pure, in the same manner as the other earthy salts. It is extremely deliquescent; liquifies at a low heat, by means of its water of crystallization; and is very

soluble in alcohol. It produces much cold, and a sharp bitter taste in the mouth.

It is composed of,

|                               |   |   |        |
|-------------------------------|---|---|--------|
| Hyperoxygenized muriatic acid | - | - | 55,2   |
| Lime                          | - | - | 28,3   |
| Water                         | - | - | 16,5   |
|                               |   |   | <hr/>  |
|                               |   |   | 100,0. |

*6th Species. Hyperoxygenized Muriate of Ammonia.*

From the property which oxygenized muriatic acid possesses of decomposing ammonia, this combination may be thought paradoxical. For, how can an acid much more active than oxygenized muriatic acid exist with ammonia, which is destroyed by the latter? But this argument may be opposed by the sum of affinities that act in either case. If the affinity of composition of oxygenized muriatic acid and of ammonia, together with the affinity of oxygenized muriatic acid for ammonia, to form oxygenized muriate of ammonia, be not more powerful than the affinity of oxygen for hydrogen, of azote for caloric, and of muriatic acid for ammonia, the divellent affinities will prevail; and this is what actually happens. But, although oxygen may be held with less force of attraction in oxygenized than in hyperoxygenized muriatic acid, yet the affinity of the latter acid for ammonia may increase in a much greater ratio, and favour the quiescent affinities. If carbonate of ammonia be poured into any earthy salt of this genus, a double decomposition takes place; and hyperoxygenized muriate of ammonia is formed. This salt is very soluble in water, and in alcohol. It is decomposed at a very low temperature, and gives out a quantity



of gas, together with a smell of hyperoxygenized muriatic acid. Such a smell is doubtless owing to the great quantity of oxygen contained in the acid; it being more than is necessary to combine with the quantity of hydrogen contained in the alkali, and therefore some of the acid is disengaged, without decomposition. All the attempts I have made to ascertain the proportions of its principles, have been fruitless. The formation and existence of this salt, as I before said, are very strong proofs of what I have advanced respecting the state in which hyperoxygenized muriates at first exist; and very fully prove the different degree of affinity exercised by each acid toward the basis.

*7th Species. Hyperoxygenized Muriate of Magnesia.*

Its chemical and physical properties are nearly the same with those of the 5th species, only that, in addition to the other bases, lime and ammonia cause a precipitate in this salt.

Its proportions are,

|                               |   |   |        |
|-------------------------------|---|---|--------|
| Hyperoxygenized muriatic acid | - | - | 60     |
| Magnesia                      | - | - | 25,7   |
| Water                         | - | - | 14,3   |
|                               |   |   | <hr/>  |
|                               |   |   | 100,0. |

*8th Species. Hyperoxygenized Muriate of Alumina.*

I put some alumina, precipitated from muriate of alumina, and well washed, but still moist, into a Woulfe's apparatus, disposed as for the other earths, and sent a current of oxygenized muriatic acid gas through the liquor. The alumina shortly disappeared; and, upon pouring sulphuric acid into the liquor, a strong smell of hyperoxygenized muriatic acid was perceivable. When I attempted to obtain the salt pure, by phosphate of silver, in the

usual way, I found nothing in solution but hyperoxygenized muriate of silver ;\* and all the hyperoxygenized muriate of alumina had been decomposed. This salt, however, appears to be very deliquescent, and is soluble in alcohol ; but I could not ascertain the proportion of its principles, because I did not obtain it sufficiently free from the simple muriate.

*9th Species. Hyperoxygenized Muriate of Silica.*

I am inclined to think this salt does not really exist. A current of oxygenized muriatic acid, sent through some silica which had been precipitated from an acid by ammonia, and collected moist from the filter, did not seem to dissolve any portion of it. In all barytes and strontia, prepared according to Mr. VAUQUELIN's method, a portion of silica from the crucibles is attacked, and taken up, by whatever acid those earths may afterwards be dissolved in ; and, in all potash of commerce, there is some silica ; but I have never perceived that any portion of this earth had been dissolved by this acid.

The very small portion of earth which, in attempts to form the different species of this genus of salts, is taken up by acids, and the still smaller portion of the salt so formed, which is really in the state of hyperoxygenized muriate, render the operation so tedious, that I have confined myself to form what was necessary to determine their analysis, in such a manner as I believe to be nearly accurate. It cannot, therefore, be expected that I make myself responsible, without a right of appeal to further experiments, for the accuracy with which the crystalline forms, and other physical properties,

\* This salt shall be particularly mentioned and described in another part of this Paper. For the present, it is sufficient to say, that it is very soluble in water ; and, in that property, as in many others, is totally different from muriate of silver.

may have been stated. It is impossible to obtain satisfactory crystals from a very small portion of salt; and I have attached myself more particularly to chemical than to physical characters, as being a much more important and certain mode of determination. For the same reason, I have not examined the combination of the new and rarer earths with this acid. But I do not doubt, that whatever chemist undertakes a further investigation of these extraordinary bodies, will be amply repaid for his labour.

I have mentioned, in a former part of this Paper, that all muriates lost a portion of their acid at a red heat. I exposed one hundred parts of muriate of potash, in a crucible, to a red heat, for some minutes, and found that they lost five. I dissolved them in water, and they manifested alkaline properties. Treated by nitrate of silver, they gave a precipitate, which shewed one per cent. less of muriatic acid, than 100 parts of the same salt that had not been exposed to fire. A violent heat may be necessary to expel the last portion of water of crystallization from certain salts, as we know particularly is the case with sulphate of lime. But, if any of the acid can be expelled at the same temperature, there is no longer any certainty. The quantity of water, as stated by different chemists, varies much; and, from some experiments I have made, I do not believe it to have been accurately determined. The method I used to ascertain this, was as follows: I exposed a given quantity of the salt to a violent heat, and noted its loss of weight. I then precipitated, by nitrate of silver; and thus knew, how much the quantity of muriatic acid which this salt contained, was less than that in a like portion which had not been exposed to heat. I subtracted the difference in this quantity, from the total loss of weight in the

salt exposed to heat ; and the remainder I considered as water. It was upon results obtained in this manner, that I founded many of the proportions I have given in this Paper.

It is stated in the tables of BERGMAN, corrected by Dr. PEARSON, that lime and strontia prefer acetous to arsenic acid. But arsenic acid can expel hyperoxygenized muriatic acid from its basis, although the acetous cannot act in the same manner ; therefore, this order of affinities is erroneous. It was not till lately, that we had potash and soda so pure as to be relied upon in delicate experiments ; and it is not surprising that we find mistakes with regard to their taking the acid from barytes, strontia, and lime. But real potash and soda both precipitate even barytes from hyperoxygenized muriatic acid. If ever it becomes easy to obtain hyperoxygenized muriate of barytes, we may prepare that earth from it in the humid way, and more near to purity, than in the method proposed by VAUQUELIN.

#### METALLIC COMBINATIONS OF MURIATIC ACID, IN ITS DIFFERENT STATES.

The action of hyperoxygenized muriatic acid upon metals, is, as may well be expected, rapid, and without disengagement of gas. It appears to dissolve every metal, not excepting gold and platina. If the metal be presented to the acid at the moment when it is disengaged from the salt, inflammation ensues ; and the phenomena of light and heat vary according to the metal ; but the salts thus produced are merely muriates. In order to form real hyperoxygenized muriates, it is necessary to take the metal in its fullest state of oxidizement, and combine it with the acid, either by double decomposition, or by passing a current of oxygenized muriatic acid gas through the oxide suspended

in water. The acid is thus separated into muriatic and hyperoxygenized muriatic acid; and, in these states, combines with the metallic oxide. The metallic hyperoxygenized muriates are different, in every respect, from the metallic muriates. Red oxide of iron is dissolved with difficulty. Oxide of copper more easily. Red oxide of lead exhibits the same appearances, during its combination with this acid, as with nitric acid. When nitric acid is poured, even in excess, upon red oxide of lead, only a part of the oxide is dissolved, unless heat be applied; and what remains becomes a blackish brown powder. But, if metallic lead be added, in a just proportion, all the red oxide disappears, and none of the brown powder is formed; neither is there any disengagement of nitrous gas, when the metallic lead is dissolved. The precipitates caused in either case, by pouring an alkali into the nitric solution, are yellow. Hence it appears, that red oxide of lead contains too much oxygen to be dissolved by nitric acid. One part of the oxide takes up the excess of oxygen, and becomes brown; while the portion which loses oxygen, becomes yellow, and is soluble in nitric acid. The presence of metallic lead promotes the total solution of the red oxide, by taking up the superabundant oxygen. I found that a current of oxygenized muriatic acid gas, like the nitric acid, dissolved a part of the red oxide, and caused the brown powder to be formed, upon which it could not act. Hyperoxygenized muriate of lead is much more soluble than muriate of lead; and the acid is very slightly attracted by the basis.

But, of all the metallic salts formed by the combination of the muriatic acid, in any of its different states, none so much deserve attention as those which have for their bases, the oxides of mercury. The nature of the salts which result from the

combination of common muriatic acid with the different oxides of this metal, has been stated in the most contradictory manner, by different chemists. But, as the knowledge of hyperoxygenized muriatic acid has thrown some light upon the true state of calomel and corrosive sublimate,\* I must beg leave to dwell at some length upon this important part of my subject.

It would be useless to repeat the opinions of the old authors, who have treated of corrosive sublimate, and of calomel. They are to be found in the works of those respective chemists, and I must refer to them for particulars.

In the Memoirs of the Academy of Sciences of Paris, for 1780, we find a Paper of Mr. BERTHOLLET, upon the causticity of metallic salts; in which he appears to think, that the acid in corrosive sublimate is in the state of what was then called dephlogisticated marine acid. In 1785, when he had examined the oxygenized muriatic acid with more care, he renounced his former opinion; and gave the reasons why he no longer adhered to it. Some late experiments of Mr. PROUST shew, that this chemist thinks as Mr. BERTHOLLET now does. And these may be ranked among the first of modern authorities.

Notwithstanding those opinions, Mr. FOURCROY, in his *Système des Connoissances chimiques*, still considers corrosive sublimate as a hyperoxygenized muriate of mercury; and designs it

\* I regret very much, that I am under the necessity of using these unmeaning terms. But the French nomenclature has made no distinction between salts formed by metallic oxides in different states of oxidizement, except by the colour, which is an extremely defective and unmeaning method. At all events, this metal is so uncomplaisant as to retain the white colour, in its different oxides combined with muriatic acid. I prefer, however, using the old name, to proposing any provisional substitute that might be found defective. This will be farther explained in *Remarks upon chemical Nomenclature*.

throughout by that name.\* This chemist, one of the founders of the methodical Nomenclature, is too well acquainted with its principles, to apply the term hyperoxygenized muriate to any thing but a combination of hyperoxygenized muriatic acid. It is evident, therefore, that he considers the portion of oxygen, which, in equal quantities of corrosive sublimate and calomel, is greater in the former, to be combined with the acid, and not with the oxide of mercury. As soon as I have stated some experiments that prove Mr. FOURCROY's opinion to be erroneous, and endeavoured to establish the analysis of corrosive sublimate and of calomel, I shall take notice of a salt hitherto unknown, which really is hyperoxygenized muriate of mercury.

I took a portion of corrosive sublimate, and precipitated by potash. The liquor was filtered; and, upon being tried, nothing but muriate of potash was found. No reagent could discover the smallest trace of hyperoxygenized muriatic acid.

Sulphuric, nitric, phosphoric, and many other acids, poured upon corrosive sublimate, did not disengage either muriatic, or hyperoxygenized muriatic acid. Nitrate of silver, poured into a solution of corrosive sublimate, gave an abundant white precipitate.

From these experiments it is evident, that muriatic acid, not hyperoxygenized muriatic acid, is combined with the oxide of mercury in corrosive sublimate.

To determine the proportions of this salt, I took one hundred parts, and precipitated by nitrate of silver. I then took another hundred, and precipitated by potash. The result of these two

\* I have said before, that this acid was talked of by many chemists, as if the existence of it had really been proved.

experiments was such as to establish the proportions of corrosive sublimate as follows :

|                  |   |   |   |       |
|------------------|---|---|---|-------|
| Oxide of mercury | - | - | - | 82    |
| Muriatic acid    | - | - | - | 18    |
|                  |   |   |   | <hr/> |
|                  |   |   |   | 100.  |

But, the acid of this salt not being charged with a superabundance of oxygen, we must look for the excess in the metallic oxide. I took 100 grains of mercury, and dissolved them in nitric acid; then poured in muriatic acid; and, at a very gentle heat, evaporated to dryness. I afterwards sublimed, in a Florence flask, the salt that remained, and obtained 143,5 of corrosive sublimate. But, 143,5 of corrosive sublimate, contain 26 of acid; which will leave 117,5 for the mercurial oxide; and, if 117,5 contain 100 of mercury, 100 of the oxide will contain 85. Therefore, the oxide of mercury, in corrosive sublimate, is oxidized at the rate of 15 per cent.

To determine the proportions in calomel, I dissolved 100 grains of it in nitric acid. The phenomena of the solution have been so accurately described by Mr. BERTHOLLET, that I shall not repeat them. I precipitated by nitrate of silver; and obtained a quantity of muriate of silver, corresponding with 11,5 of muriatic acid. The oxide of mercury I obtained apart. Therefore, calomel is composed of,

|                  |   |   |   |        |
|------------------|---|---|---|--------|
| Oxide of mercury | - | - | - | 88,5   |
| Muriatic acid    | - | - | - | 11,5   |
|                  |   |   |   | <hr/>  |
|                  |   |   |   | 100,0. |

To ascertain the state of oxidizement of the oxide in calomel, I took 100 grains, and boiled them with nitro-muriatic acid;



then evaporated very slowly, and sublimed as above. The calomel was totally converted into corrosive sublimate, and weighed 113. But 113 of corrosive sublimate contain 20,3 of muriatic acid, of which, 11,5 were originally in the calomel. The total addition of weight was 13. But the quantity of acid in these 13, amounts to  $20,3 - 11,5 = 8,8$ . Therefore,  $13 - 8,8 = 4,2$ , remain for that part of the additional weight which is oxygen. On the other hand, 100 of calomel contain the same quantity of mercury as 113 of corrosive sublimate, = 79. These 79, with 11,5 of acid, are equal to 90,5, and leave 9,5 for the quantity of oxygen contained in calomel. It would appear, from these experiments, that corrosive sublimate contains 6,5 per cent. more acid, and but 2,8 per cent. more oxygen, than calomel. But this quantity of oxygen is combined with a much greater proportion of mercury; and forms an oxide of a very different degree of oxidizement. For,  $88,5 : 9,5 :: 100 : 10,7$ . Therefore, we may establish the following comparative table.

| CALOMEL.  |                             |      |              | CORROSIVE SUBLIMATE.  |                             |    |            |
|---|-----------------------------|------|--------------|---|-----------------------------|----|------------|
| The oxide of mercury in calomel is composed of, |                             |      |              | The oxide of mercury in corrosive sublimate is composed of, |                             |    |            |
| Mercury   | -                           | -    | 89,3         | Mercury   | -                           | -  | 85         |
| Oxygen  | -                           | -    | 10,7         | Oxygen  | -                           | -  | 15         |
|   |                             |      | <hr/> 100,0. |   |                             |    | <hr/> 100. |
| And calomel is composed of,                     |                             |      |              | And corrosive sublimate is composed of,                     |                             |    |            |
| Mercury 79                                      | { oxide of }<br>{ mercury } | 88,5 |              | Mercury 69,7  | { oxide of }<br>{ mercury } | 82 |            |
| Oxygen 9,5                                      |                             |      |              | Oxygen 12,3   |                             |    |            |
| Muriatic acid                                   | -                           | -    | 11,5         | Muriatic acid   | -                           | -  | 18         |
|   |                             |      | <hr/> 100,0. |   |                             |    | <hr/> 100. |

These proportions are different from those given by LEMERY, GEOFFROY, BERGMAN, &c. But, without calling in question the accuracy and skill of these chemists, it is fair to assert, that the pure materials used by modern chemists, are more likely to lead to sure results, than the impure reagents of the ancients.

In these salts we find another instance, that, in proportion as metallic oxides contain a greater quantity of oxygen, they require a greater quantity of acid to enter into combination with them.

The method I have followed, to ascertain the proportions just stated, may appear, at first view, not to be the shortest that I might have adopted. But I have tried others, and have found none so accurate. It is impossible, synthetically, to convert a given quantity of mercury into calomel, in such a manner as to be certain that none of it is in a different state from that required. And, if we would attack calomel analytically, the action of the alkalis, without which we cannot proceed, is such as to alter the nature of the oxides. I have also made many comparative experiments, by dissolving calomel in nitro-muriatic acid, (which converted it into corrosive sublimate,) and then precipitating by ammonia; but I have not found these trials so successful as those I have described. The nature of the precipitate from corrosive sublimate by ammonia, certainly differs, according to the excess of acid that may be present; and mercury seems to have the power of existing in many degrees of combination with oxygen. The only precaution absolutely necessary, in this mode of operating, is, that while the mercurial salt is in an open vessel, it should not be exposed to a degree of heat capable of volatilizing any part of it.

The quantity of mercury ordered in the London Pharmacopoeia, to convert corrosive sublimate into calomel, is 9 pounds

of mercury for every 12 pounds of corrosive sublimate. But, from the above experiments, it would appear, that a smaller quantity of mercury might strictly answer. However, from the results of minute investigation, we should not conclude too hastily upon preparations on the great scale; and, I rather think, that the excess of mercury ordered by the Pharmacopoeia is a useful precaution.

In my experiments, I attempted to reduce, by means of copper, iron, or zinc, the mercury contained in the mercurial salts. Iron did not answer the purpose: zinc precipitated the mercury a little better; and copper produced a change which I did not expect. If a bit of copper be put into a solution of corrosive sublimate, a white powder shortly falls to the bottom; and that powder is calomel. When washed, it does not contain an atom of copper, nor of corrosive sublimate.

Before I conclude these considerations, I must say, that whether calomel be prepared in the dry or in the humid way,\* it does not seem to differ chemically; nor does it contain any

\* By the humid way, I do not mean precisely the method of SCHEELE. That chemist desires us to boil the acid with the mercury, after they have ceased to act upon each other at a low temperature. By this method, the nitric acid takes up an excess of mercurial oxide; and the nitrate of mercury thus formed, precipitates by water. Therefore, when this nitrate of mercury is poured into the dilute solution of muriate of soda, according to the formula of SCHEELE, the action, on the part of the solution, is twofold.

1st. The water acts upon one part, and precipitates an oxide, or rather an insoluble subnitrate of mercury. And,

2dly. A double decomposition takes place between the nitrate of mercury and the muriate of soda. It is with reason, that the medical world have supposed the calomel of SCHEELE to be different from that prepared in the humid way; for it is, in fact, calomel, plus an insoluble subnitrate of mercury. In the first part of SCHEELE'S

sensible portion of water of crystallization. The same may be said of corrosive sublimate.

It now remains to speak of the real hyperoxygenized muriate of mercury. I passed a current of oxygenized muriatic acid gas through some water, in which there was red oxide of mercury.\* After a short time, the oxide became of a very dark brown colour; and a solution appeared to have taken place. The current was continued for some time; and, when I thought that a sufficient quantity of the oxide had been dissolved, I stopped the operation. The liquor was evaporated to dryness; and the salt was thus obtained. There evidently was in the mass a great proportion of corrosive sublimate, as might be expected, from what I had observed to take place in the formation of the other salts of this acid; but, by carefully separating

process, there is disengagement of nitrous gas, together with oxidizement and solution of some of the mercury. When he boils the acid upon the remaining mercury, there is no further disengagement of gas; yet more mercury is dissolved. The nitrate of mercury, therefore, rather contains an oxide less oxidized after ebullition than before it. The true difference is in the subnitrate of mercury, precipitated, as I before said, by the water in which the muriate of soda was dissolved. And the orange coloured powder, which remains after an attempt to sublime SCHEELÉ's calomel, is to be attributed to the same cause. To prepare calomel in the humid way, uniform as to itself, and in all respects similar to that prepared in the dry way, it is necessary, either to use the nitric solution before it has boiled, or to pour some muriatic acid into the solution of muriate of soda, previously to mixing it with the boiled solution of nitrate of mercury. In the first case, no precaution is necessary; and, in the latter, the oxide of mercury, which the nitrate of mercury has, by boiling, taken up in excess, finds an acid which is ready to saturate it. All the mercurial oxide being thus converted into calomel, none of that subnitrate of mercury can be present.

The objections made by a medical gentleman against SCHEELÉ's calomel, when this Paper was read before the Royal Society, led me to reconsider the subject, and to undertake the investigation detailed in this note.

\* I used either of the red oxides of mercury, indiscriminately.

the last formed crystals, I could pick out some hyperoxygenized muriate of mercury. I then crystallized it over again; and, in this manner, I obtained it nearly pure. This salt is more soluble than corrosive sublimate: about four parts of water retain it in solution. The shape of its crystals, I cannot well determine. When sulphuric, or even weaker acids, are poured upon it, it gives out the usual smell of hyperoxygenized muriatic acid; and the liquor becomes of an orange colour. This is a sufficient proof, that corrosive sublimate is not a hyperoxygenized muriate of mercury.

I have just mentioned that, in the formation of this salt, the oxide of mercury, which was not dissolved by the acid, became of a very dark brown colour. I procured a portion of this oxide, which seemed different from the red oxide. It however retained the form, and the crystalline appearance, of the latter. It was soluble in nitric acid, without disengagement of gas; and was precipitated from it, in a yellow oxide, by all the alkalis, except ammonia. It formed corrosive sublimate with muriatic acid; and the precipitate by the alkalis, was the same as that from corrosive sublimate, made with the red oxide. Yet I am inclined to think, that the dark brown oxide differs in some essential point from the red; but I have not yet made sufficient experiments to prove this opinion. At all events, the present object being to examine the mercurial oxides only as combined with muriatic acid, it would be foreign to the purpose, to enter upon too minute an investigation of the other states of the metal. This, and some other objects hinted at in this Paper, must be reserved for future inquiry.

In treating the earthy hyperoxygenized muriates with phosphate of silver, as I mentioned before, I observed that the liquor

sometimes contained in solution oxide of silver; which, upon examination, I found to be combined with hyperoxygenized muriatic acid. As the salt which is thus formed is different, in every respect, from simple muriate of silver, it may be of some importance to consider it with attention. In the first place, it will afford the most convincing proof of the difference between muriatic and hyperoxygenized muriatic acid; and, in the next place, it particularly deserves to be remarked, for possessing, in the most eminent degree, one of the great characteristic features of the genus to which it belongs. Hyperoxygenized muriate of silver is soluble in about two parts of warm water; but, by cooling, it crystallizes in the shape of small rhomboids, opaque and dull, like nitrate of lead or of barytes. It is somewhat soluble in alcohol. Muriatic acid decomposes it; as does nitric, and even acetous acid: but the result of this decomposition is not, as might be expected, nitrate or acetite of silver. At the moment that the acid is expelled from hyperoxygenized muriate of silver, a reaction takes place among its elements: oxygen is disengaged; and the muriatic acid remains in combination with the oxide of silver. If this fact be compared with the manner in which nitric and acetous acids act upon hyperoxygenized muriate of potash, it will give a strong proof of the proportionate affinities of all these acids for oxide of silver, in comparison with that which they exercise towards the alkali.

Hyperoxygenized muriate of silver, when exposed to a very moderate heat, begins by melting, and then gives out a considerable quantity of oxygen gas, with effervescence; and muriate of silver remains behind. These phenomena however differ much, according to the degree of heat applied. When hyperoxygenized muriate of silver is mixed with about half its weight

of sulphur, it detonates in the most violent manner; and does not, like hyperoxygenized muriate of potash, require the addition of charcoal, to possess a very great force of explosion. The slightest pressure is sufficient to cause this mixture to detonate; and I think I shall be within bounds, when I state, that half a grain of hyperoxygenized muriate of silver, with a quarter of a grain of sulphur, explodes with a violence at least equal to five grains of hyperoxygenized muriate of potash, with the due quantities of sulphur and charcoal. The flash is white and vivid, and is accompanied by a sharp and quick noise, like the fulminating silver so ably described by Mr. HOWARD; and the silver is reduced to the metallic state, and vaporized.

I think it right to add a few remarks, upon what I have termed the proportionate affinities of acids and of bases, one for the other. It is a law, not indeed universally, but frequently observed, and very well worthy of consideration, that the acids are attracted by metallic oxides, in a very different order from that in which they are disposed to unite to alkaline and earthy bases.

Nitric acid, which holds so high a place in the order of affinities for alkalis, is expelled from metallic oxides by most acids. Phosphoric, fluoric, all the vegetable acids, except two or three, and the animal acids, attract the latter bases more strongly. Nay, we shall find, upon an attentive examination, that acids commonly attract metallic oxides, in the inverse ratio of their action upon metals, or, in other words, in proportion to their own affinity of composition. Thus, the phosphoric and fluoric acids sometimes rank before the sulphuric; and the nitric, as I before said, is generally very low. Hyperoxygenized muriatic acid seems to follow the same rule; and takes its

place, in the order of affinities for metallic oxides, after many of those acids which it can expel from earths and alkalis.

The other hyperoxygenized muriates, I have not yet sufficiently examined. I shall, however, mention at present, that I have ascertained the muriatic salts, formerly known by the strange name of *butters of the metals*, to be muriates, and not hyperoxygenized muriates; and the extraordinary proportion of oxygen, to be combined, not in the acid, but in the metallic oxide.

In the course of different experiments, I have known hyperoxygenized muriatic acid to be formed in two cases, where I could not have expected it.

In the analysis of some menachanite from Botany Bay, given to me last year by the President of the Royal Society, I observed, that while the oxide of titanium was precipitated from the muriatic acid in which it was dissolved, the excess of oxygen in the oxide passed over to the muriatic acid and the potash, already in the liquor, and that hyperoxygenized muriate of potash was formed. I have attempted the same experiment with black oxide of manganese, but could not succeed.

There is, however, a still more extraordinary formation of this acid, in the distillation of nitro-muriatic acid upon platina. Oxygen is absorbed by the metal; yet, not only oxygenized, but also hyperoxygenized muriatic acid is formed. I have repeated the experiment several times; and am well convinced of the fact, however contrary to theory it may appear. I have tried the action of oxygenized muriatic acid upon nitric acid, in the hopes of forming hyperoxygenized muriatic acid; but there was no action to this effect among their elements.

The fact of the production of a peculiar gas, by the distilla-



tion of nitro-muriatic acid upon platina, has been observed by Mr. DAVY, in his *Researches*.\* But, as hyperoxygenized muriatic acid was not known at that time, he could not say the real nature of that gas. Had Mr. DAVY carried his ingenious experiments a little farther, we should have been much earlier acquainted with the last degree of oxygenizement of muriatic acid.

Mr. BERTHOLLET terminates his Paper upon hyperoxygenized muriate of potash, by saying, that he will consider muriatic acid as the radical; oxygenized muriatic acid, as corresponding with sulphureous and nitrous acid; and the acid which he conjectured to exist in this salt, as corresponding with sulphuric and nitric acid. I shall now conclude, by stating the arguments in favour of each denomination, and the analogies upon which they are founded.

Muriatic acid is for us a simple body; but it has acid properties of the strongest kind; therefore, from analogy, we suppose it to contain oxygen. But may not this be too hasty a conclusion? Are we not very doubtful concerning the existence of oxygen in prussic acid? And are we not, on the contrary, certain that sulphurated hydrogen, which possesses many of the characteristics of acids, does not contain any? Of the oxygenizement of fluoric and boracic acids, we have no proof: but then we cannot affirm that any one of these acids exists in three states of combination with oxygen; and the muriatic is the only radical of which we admit this fact. We must not, however, pretend to limit the number or degrees of combinations between combustible bodies and oxygen; but we can

\* Dr. PRIESTLEY, also, mentions a peculiar gas, produced by distilling a solution of gold in *aqua regia*.

speak, with certainty, only of those things which are proved. Besides its acid properties, this substance has others, common to oxygenizable bodies. With 16 of oxygen, it forms an acid, which, in many of its properties, is to its radical what the sulphureous is to sulphur. Like the sulphureous, it is volatile; has little attraction for salifiable bases; destroys vegetable blues; and is capable of further oxygenizement. With 65 of oxygen, it becomes more fixed, like sulphuric acid; has a stronger affinity for salifiable bases; and acquires more truly acid properties. Upon these considerations, I submit to the chemical world, whether, in the present state of our knowledge, it be not more philosophical to say,

|   |                |                                |
|---|----------------|--------------------------------|
| Muriatic radical, or<br>some single word<br>of the same import, | } instead of { | Muriatic acid;                 |
| Muriatous acid,   |                | Oxygenized muriatic acid;      |
| Muriatic acid,  |                | Hyperoxygenised muriatic acid. |

I am fully aware that, at first sight, this may appear extraordinary; and the more so, as we have no positive facts that prove muriatic acid to be a simple body. All we can, therefore, consider fairly, is, in favour of which appellation does the sum of analogies seem to preponderate. And, to give the cause a candid investigation, we should begin by considering, whether the presence of oxygen in all bodies that have acid properties, has been rigidly demonstrated; and not determine by this law of the French chemistry, till we are well convinced it has not been too generally assumed.

If a nomenclature be not subservient to the uses of science, and does not keep pace with its progress, the relation between

substances and their names will become so relaxed, that confusion will be brought about, by the very means we take to avoid it; and if, while we continue to extend our acquaintance with chemical bodies, nomenclature remains confined within its former limits, the bonds that unite these two parts of the science must inevitably be broken.